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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C07C 19/08, 17/26, 17/00	A1	(11) International Publication Number: **WO 95/05353** (43) International Publication Date: 23 February 1995 (23.02.95)

(21) International Application Number: PCT/US94/08986

(22) International Filing Date: 10 August 1994 (10.08.94)

(30) Priority Data:
08/107,261 16 August 1993 (16.08.93) US

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(81) Designated States: AM, AU, BB, BG, BR, BY, CA, CN, CZ, FI, GE, HU, JP, KG, KP, KR, KZ, LK, LT, LV, MD, MG, MN, NO, NZ, PL, RO, RU, SI, SK, TJ, TT, UA, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD).

Published
With international search report.

(54) Title: PROCESS FOR COMBINING CHLORINE-CONTAINING MOLECULES TO SYNTHESIZE FLUORINE-CONTAINING PRODUCTS

(57) Abstract

Alternatives to chlorofluorocarbons are provided by the inventive process for synthesizing fluorine-containing products $RCF_bH_{c+a-1}H_{f+d-1}F_eCR'$ which may optionally be carried out without the isolation of any intermediate in a single reactor or a series of reactors. The process comprises combining chlorine-containing reactants $RCCl_aF_bH_c$ and $R'CCl_dF_eH_f$ in the presence of hydrogen and at least one catalyst. R and R' are chosen from the group consisting of halogens, halogenated hydrocarbons, and hydrocarbons, and at least one of R and R' contains fluorine, a and d are integers from 1 to 3, b, c, e, and f are integers from 0 to 2, the sum of a, b, and c is 3, and the sum of d, e, and f is 3, and further treating the coupled products in the presence of an optional catalyst with hydrogen or a fluorinating agent.

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Process for Combining Chlorine-Containing Molecules to Synthesize Fluorine-Containing Products

BACKGROUND OF THE INVENTION

The global effort to replace chlorofluorocarbons with alternative products has resulted in an intensive search for such products. Currently, chlorofluorocarbons (CFCs) are widely used for applications such as blowing agents, solvents, refrigerants, propellants, cooling fluids, working fluids, and rinse agents. Unfortunately, CFCs are sufficiently stable to diffuse into the stratosphere, where they are eventually decomposed into reactive chlorine-containing radicals. These radicals have been found to catalytically decompose the protective ozone layer.

SUMMARY OF THE INVENTION

Alternatives to chlorofluorocarbons are provided by the inventive process for synthesizing fluorine-containing products $RCF_bH_{c+a-1}H_{f+d-1}F_eCR'$ which may optionally be carried out without the isolation of any intermediate in a single reactor or a series of reactors. The process comprises combining chlorine-containing reactants $RCCl_aF_bH_c$ and $R'CCl_dF_eH_f$ in the presence of hydrogen and at least one catalyst. R and R' are chosen from the group consisting of halogens, halogenated hydrocarbons, and hydrocarbons, and at least one of R and R' contains fluorine, a and d are integers from 1 to 3, b, c, e, and f are integers from 0 to 2, the sum of a, b, and c is 3, and the sum of d, e, and f is 3, and further treating the coupled products with hydrogen or a fluorinating agent. Examples of the chlorine-containing reactants, $RCCl_aF_bH_c$ and $R'CCl_dF_eH_f$, are $FCl_2C\text{-}CClF_2$, $F_3C\text{-}CCl_3$, $F_3C\text{-}CF_2\text{-}CCl_3$,

$F_3C-CF_2-CHCl_2$, CF_2Cl_2, $F_3C-CHCl_2$, F_3C-CH_2Cl. Examples of the fluorine-containing product, $RCF_bH_{c+e-1}H_{f+d-1}F_eCR'$, are $F_3C-CH_2-CH_2-CF_3$, $F_2CH-CHF-CHF-CHF_2$, $F_3C-CH_2-CH_2-CH_2-CF_3$, $F_3C-CH_2-CHF_2$, and $F_3C-CF_2-CH_2-CH_2-CF_2-CF_3$.

BRIEF DESCRIPTION OF THE FIGURES

Figure 1 is the gas chromatographic spectrum of the products of the synthesis of CFC-151-10 from CFC-215. The ordinant shows the total ion current from the mass spectroscopy detector and the abscissa represents the retention time of the gas chromatograph.

Figure 2 shows the mass spectroscopy fragmentation pattern for one of the products in the spectrum in Figure 1.

Figure 3 provides an interpretation of the mass spectroscopy fragmentation pattern of Figure 2 to verify the intermediate product composition.

Figure 4 is the gas chromatographic spectrum of the products of the synthesis of HFC-55-10 from CFC-215.

Figure 5 is the mass fragmentation pattern for the peak in Figure 4 that has been assigned to HFC-55-10.

DETAILED DESCRIPTION OF THE INVENTION

The detriments to the use of chlorofluorocarbons can be abated by substituting relatively more fluorine and less chlorine into the compounds and by introducing hydrogen to make the compounds more reactive at lower altitudes. Substituting fluorine for the chlorine of traditional CFC products decreases the boiling point. It is therefore generally necessary to increase the number of carbon atoms in the molecule to achieve the product boiling points required by the applications. The synthesis of the traditional CFC molecules such as dichl rodifluoromethane (CFC-12),

chlorotrifluoromethane (CFC-13), and trichlorofluoromethane (CFC-11) are relatively easy and can be produced in concert with each other. However, synthesizing the more advanced higher carbon number hydrofluorocarbons (HFC's) greatly complicates the manufacturing process. This invention discloses an efficient method for manufacturing advanced HFC and other products such as blowing agents, solvents, refrigerants, propellants, cooling fluids, working fluids, and rinse agents.

The inventive process involves preparing the fluorine-containing product $RCF_bH_{c+a-1}H_{f+d-1}F_eCR'$ by coupling two chlorine-containing reactants, $RCCl_aF_bH_c$ and $R'CCl_dF_eH_f$ in the presence of hydrogen and a first catalyst, and further treating the coupled products with hydrogen or a fluorinating agent, optionally in the presence of a second catalyst, to form the fluorine-containing product. R and R' are chosen from the group consisting of halogens, halogenated hydrocarbons, and hydrocarbons, and at least one of R and R' contains fluorine, a and d are integers from 1 to 3, b, c, e, and f are integers from 0 to 2, the sum of a, b, and c is 3, and the sum of d, e, and f is 3. R and R' may have functional groups or other moieties that contain oxygen, nitrogen, sulfur, phosphorous, iodine, bromine, or other components which are not directly involved in the coupling. These functional groups or moieties may be used to enhance application properties or to mask certain reactive sites during the synthesis process. Examples of R and R' are $-CF_3$, $-CCl_2F$, $-CF_2CF_3$, $-F$, or $-Cl$, chlorine- and fluorine-containing alkyl groups, chlorine- and fluorine-containing aromatic compounds. There is no known upper limit t the m l cular weight of th reactants.

The invention also contemplates a process for preparing the fluorine-containing products comprising combining the two chlorine-containing reactants in the presence of hydrogen and a catalyst to form at least one intermediate, $RCF_gH_hCl_iCl_jH_kF_lR'$, and subsequently treating the intermediate in the presence of an optional second catalyst with either a fluorinating agent, or with hydrogen and a catalyst to form the fluorine-containing product, wherein the sum of g, h, and i is an integer from 1 to 2, the sum of j, k, and l is an integer from 1 to 2; g, h, i, j, k, and l are integers from 0 to 1.

The catalyst used in the coupling reaction is a group VIII metal and may be chosen from the group consisting of nickel, ruthenium, rhodium, palladium, osmium, iridium, platinum, iron, or cobalt. The catalyst may be dispersed on a high surface area support such as alumina, carbon, chromium oxide, chromium oxyfluoride, chromium fluoride, or may be used as an unsupported high surface area metal oxide, metal fluoride, or elemental metal. The preferred catalyst for the coupling reaction is a reduced ruthenium catalyst dispersed on a high surface area support such as alumina or carbon.

The molar ratio of hydrogen to reactant in the coupling reaction may vary from 0.5 to about 10. the pressure may vary from ambient to about 1,000 psig, and the liquid hourly space velocity (LHSV) may vary from about 0.1 to about 10. The reaction may be carried out at temperatures in the range of from about 20°C to about 500 °C, preferably in the range of from about 100°C to about 250°C, and most preferably in the range of from about 150°C to about 200°C. Substantial

reaction occurs to produce substantial conversion and selectivity at temperatures below 200°C.

Further treating the fluorine-containing product with hydrogen and an optional second catalyst will reduce the product to a hydrofluorocarbon. Treatment with a fluorinating agent will produce a hydrofluorocarbon or perfluoroalkane. The catalyst selected for the hydrogen treatment may be the same catalyst used for the coupling reaction or may be selected from metals known to provide substantial hydrogenolysis activity on high surface area supports such as alumina or carbon. The most preferred metals include group VIII metals such as platinum, cobalt, nickel, iridium, ruthenium and palladium which may be modified by promoters including but not limited to rhenium, iridium, cobalt, and nickel. Alternatively, the metals may be attenuated by components including but not limited to sulfur, germanium, or tin. The hydrogenation reaction may be carried out at a liquid hourly space velocity (LHSV) in the range of from about 0.05 to about 10, preferably in the range of from about 0.2 to about 1.0, a temperature in the range of from about 20°C to about 550°C, preferably 100°C to about 350°C, and a pressure in the range of from about 0 psig to about 2000 psig, preferably about 30 psig to about 300 psig.

The fluorinating agent may be chosen from the group consisting of hydrogen fluoride, uranium fluoride, elemental fluorine, or fluoride salts. Examples of fluoride salts are potassium fluoride, sodium fluoride, and cesium fluoride. The catalysts for hydrofluorination may be a chromium-based heterogeneous system, a catalyst system based on liquid-phas c ntact with antimony p ntahalide in

hydrogen fluoride, or electrofluorination in hydrogen fluoride. The hydrofluorination reaction may be carried out at a liquid hourly space velocity (LHSV) in the range of from about 0.05 to about 5, preferably in the range of from about 0.1 to about 1.0, a temperature in the range of from about 100°C to about 450°C, preferably 250°C to about 350°C, and a pressure in the range of from about 0 psig to about 500 psig, preferably about 50 psig to about 200 psig. Where the fluorinating agent is elemental fluorine, however, the reaction is preferably carried out without a catalyst and at temperatures in the range of from about -50°C to about +100°C, preferably -20°C to about +20°C.

In addition, the acid nature of the support may be removed with a basic substance such as an alkali metal to avoid unwanted acid-catalyzed isomerizations. For example, lithium, sodium, or potassium may be added to the alumina for either or both of the reactions.

The novel fluorine-containing products may be synthesized by first coupling the chlorine-containing reactants in the presence of hydrogen and a catalyst to form an intermediate compound, isolating the intermediate by procedures such as distillation, membranes, absorbents or other separation devices, and then treating the intermediate with hydrogen, a fluorinating agent such as elemental fluorine, or a hydrofluorinating agent such as hydrogen fluoride with an optional second catalyst to form the fluorine-containing product. Alternatively, the fluorine-containing product may be synthesized and further treated with hydrogen or a fluorinating agent without isolation of an intermediate in a single reactor or a series of reactors. A heat exchanger may be used with th s ries of r actors t adjust t mp ratur .

The reactions leading to the fluorine-containing products produce HCl and are therefore very exothermic. The hydrochloric acid may be neutralized, recovered as a byproduct, discarded, or converted into chlorine using the Deacon reaction for recycle or sale. The excess heat must be managed in order to control the reactor temperature profile. Although very high reactor temperatures lead to high reaction rates, they also lead to loss of product selectivity. Heat dispersing techniques such as quench hydrogen, inert fluids such as nitrogen, and/or product recycle streams may be used to provide adequate thermal management.

As discussed above, fluorine-containing products may be synthesized by combining a chlorine-containing reactant using an excess of hydrogen and a suitable catalyst to form an intermediate, then a product, or to form a product directly. An intermediate may be a saturated compound or an olefin. An olefin may be hydrogenated to form the desired product using catalytic hydrogenation. Examples of possible syntheses are as follows:

Synthesis of HFC-356mff from CFC-113. HFC-356mff (1,1,1,4,4,4-hexafluorobutane) may be synthesized using CFC-113 (1,1,2-trichloro-1,2,2-trifluoroethane) in the presence of a catalyst sufficiently acidic to cause an isomerization to CFC-113a. For example, the catalyst CrF_3 may be physically mixed in with a ruthenium catalyst or itself impregnated with ruthenium. The entire reaction may be carried out without the isolation of any intermediate in a single reactor or a series of reactors. CFC-113 rearranges to form CFC-113a and then couples to form the desired HFC-356mff.

Synthesis of HFC-356pee from CFC-113. HFC-356pee (1,1,2,3,4,4-hexafluorobutane) may be synthesized by coupling CFC-113 (1,1,2-trichloro-1,2,2-trifluoroethane) to form a four-carbon olefin (CFC-1316 lyy, $F_2ClCCF{=}CFCClF_2$) as was HFC-356mff above. The four-carbon olefin is hydrogenated to form the desired product using catalytic hydrogenation.

Synthesis of HFC-356mff from CFC-113a. HFC-356mff (1,1,1,4,4,4-hexafluorobutane) may be synthesized by coupling CFC-113a (1,1,1-trichloro-2,2,2-trifluoroethane) without isolating any intermediates in a single reactor or a series of reactors.

Synthesis of HFC-356mff from CFC-113a. HFC-356mff (1,1,1,4,4,4-hexafluorobutane) may be synthesized by coupling CFC-113a (1,1,1-trichloro-2,2,2-trifluoroethane) to form the four-carbon olefin CFC-1316mxx ($F_3CCCl{=}CClCF_3$). The olefin may then be hydrogenated to form HFC-356mff or may be converted to a second intermediate, HCFC-336 ($F_3CCHClCHClCF_3$). The second intermediate can then be reacted with hydrogen to produce the desired HFC-356mff product.

Synthesis of HFC-338 from CFC-113a. HFC-338 (1,1,1-2,3,4,4,4-octafluorobutane) may be synthesized by coupling CFC-113a (1,1,1-trichloro-2,2,2-trifluoroethane) to form a four-carbon olefin intermediate (CFC-1316mxx, $F_3CCCl{=}CClCF_3$). The intermediate may then be hydrogenated to form a second intermediate product (HCFC-336, $F_3CCHClCHClCF_3$) using catalytic hydrogenation and relatively mild conditions. The second intermediate can then be reacted with HF over a suitable catalyst such as a Cr-based het rogene us system, a catalyst system based on liquid-phase c ntact with antimony p ntahalid in HF,

or electrofluorination in HF to produce the desired HFC-338 product. HFC-356mff may also be co-produced with HFC-338 by coupling CFC-113a and the ratio of the products can be adjusted by varying the reactor process conditions. Co-production is expected to enhance the economics relative to the production of either product alone.

Synthesis of HFC-356mff and/or FC-31-10 from CFC-113a. HFC-356mff and/or FC-31-10 (perfluorobutane) may be synthesized by coupling CFC-113a to produce a substantial amount of CFC-316 ($F_3CCCl_2CCl_2CF_3$). CFC-316 can then be electrofluorinated in HF to produce FC-31-10 or treated with hydrogen to produce HFC-356mff. HFC-356mff and FC-31-10 may be co-produced by coupling CFC-316 and the ratio of the products can be adjusted by varying the reactor process conditions.

Synthesis of HFC-346mdf from CFC-113a. HFC-346mdf (1,1,1,4,4,4-hexafluoro-2-chlorobutane) may be synthesized by coupling CFC-113a (1,1,1-trichloro-2,2,2-trifluoroethane) to form the four-carbon olefin CFC-1316mxx ($F_3CCCl{=}CClCF_3$). The olefin may then be partially hydrodechlorinated to form HFC-346mdf.

Synthesis of CFC-1418 from CFC-113a and CFC-215. CFC-1418 (2,3-dichlorooctafluoro-2-pentene) may be synthesized by reductively coupling CFC-113a and CFC-215 ($CF_3CF_2CCl_3$). CFC-1418 may be further treated, e.g., hydrodechlorinated and/or fluorinated, to form other products, e.g., CFC-43-10 (1,1,1,2,2,3,4,5,5,5-decafluoropentane), HFC-458 (1,1,1,2,2,5,5-octafluoropentane), or FC-41-12 (perfluoropentane).

Synthesis of CFC-1418 from CFC-113a and CFC-225. CFC-1418 may be synthesized by reductively coupling CFC-113a and CFC-225 (1,1-dichloro-2,2,3,3,3-

pentafluoropropane). CFC-1418 may be further treated as discussed above.

Synthesis of HFC-245fa from CFC-12 and CFC-113a. HFC-245fa (1,1,1,3,3-pentachloropropane) may be synthesized by coupling CFC-12 and CFC-113a to form a three-carbon olefin (CFC-1215, $F_3CCCl=CF_2$). The olefin is hydrogenated to form the desired product using catalytic hydrogenation. As the reductive coupling reaction of CFC-113a is much faster than the reductive coupling reaction for CFC-12, a high ratio of CFC-12:CFC-113a is preferred in the charge stock to promote cross-coupling and reduce coupling of two CFC-113a molecules.

Synthesis of HFC-356mff and/or HFC-338 from CFC-123. HFC-356mff and/or HFC-338 may be synthesized by coupling CFC-123 (1,1-dichloro-2,2,2-trifluoroethane) to form a four-carbon intermediate (HCFC-336, $F_3CCHClCHClCF_3$). The intermediate is then hydrodechlorinated to form the desired product using catalytic hydrogenation.

Synthesis of HFC-245fa from CFC-12 and CFC-123. HFC-245fa may be synthesized by coupling CFC-123 (1,1-dichloro-2,2,2-trifluoroethane) and CFC-12 (dichlorodifluoromethane). This molecule is coupled to form a three-carbon olefin (HFC-1225, $F_3CCH=CF_2$). The three-carbon olefin is then hydrogenated to form the desired product using catalytic hydrogenation. As the reductive coupling reaction of CFC-123 appears to be much faster than the reductive coupling reaction of CFC-12, a high ratio of CFC-12:CFC-123 would be preferably used in the charge stock to promote cross-coupling and reduce coupling of two CFC 123 molecules.

Synthesis of HFC-356mff from HCFC-133a. HFC-356mff may be synthesized by reductively coupling HCFC-133a (1-chloro-2,2,2-trifluoroethane).

Synthesis of HCFC-558 and HFC-578 from CFC-214. HCFC-558 ($ClCF_2CF_2CH_2CH_2CF_2CF_2Cl$) and HFC-578 ($HCF_2CF_2CH_2CH_2CF_2CF_2H$) may be synthesized by coupling CFC-214 ($ClCF_2CF_2CCl_3$) to form a six-carbon olefin (CFC-1518, $ClCF_2CF_2CCl{=}CClCF_2CF_2Cl$). The olefin may then be hydrogenated to form the desired products using catalytic hydrogenation.

Synthesis of HFC-55-10 from CFC-215. HFC-55-10 (1,1,1,6,6,6-hexafluorohexane) may be synthesized by coupling CFC-215 ($CF_3CF_2CCl_3$) to form a six-carbon olefin (CFC-151-10, $F_3CF_2CCl{=}CClCF_2CF_3$). The olefin is then hydrogenated to form the desired product using catalytic hydrogenation.

Synthesis of CFC-51-10 from CFC-215. CFC-51-10 (3,3,4,4-tetrachlorodecafluorohexane) may be synthesized by reductively coupling CFC-215. CFC-51-10 may then be further treated, e.g., hydrodechlorinated, to form another product, e.g., CFC-55-10.

Synthesis of HFC-55-10 from CFC-225. HFC-55-10 may be synthesized by reductively coupling CFC-225 (1,1-dichloro-2,2,3,3,3-pentafluoropropane) to form the intermediate HFC-153-10 (1,1,1,2,2,5,5,6,6,6-decafluoro-3-hexene). The olefin is then hydrogenated to form the desired product using catalytic hydrogenation.

Example 1 - Synthesis of HFC-356mff from CFC-113a

The following data were obtained using a microreactor consisting of a syringe pump driven liquid feed system, a mass flow meter controlled hydrogen addition system, a reactor, a reactor outlet effluent sampling system, and an n-lin / ff-lin GC/MS

analytical system. The area under the peaks in a plot of the total ion current (TIC) from the GC/MS as a function of retention time provides an estimate of the concentration of the effluent from the reactor. CFC-113a was the reactant and the catalyst used was 2% ruthenium on carbon. The results shown in Table I provide the product analysis. The results show a high yield to CFC 1316mxx, which is the desired four-carbon intermediate. These data were obtained at 2 LHSV, 10:1 H_2:CFC-113a molar ratio, and 30 psig pressure as a function of temperature. It can be clearly seen that a high yield of CFC-1316mxx can be obtained. Further refinements in the process conditions will lead to an increasing concentration of this product. The product CFC-1316mxx may be further subjected to catalytic hydrogenation to obtain the desired HFC-356mff.

TABLE I - Area % from GC/MS

	90°C	125°C	225°C
HFC-143a[1]	0.34	19.71	19.83
CFC-1326[2]	0	2.67	6.74
CFC-1316[3]	9.15	58.22	30.22
CFC-316	1.46	0	0
CFC-113a	88.41	0	0
CFC-123	0	5.76	3.79

[1] F_3CCH_3
[2] CFC-1326 ($F_3CClC{=}CHCF_3$)
[3] CFC-1316mxx ($F_3CClC{=}CClCF_3$)

Example 2 - Synthesis of HFC-356mff in a Single Reactor from CFC-113a

HFC-356mff was synthesized by loading a single reactor sequentially with 10 mL of a 2% ruthenium catalyst on a carbon support and 10 mL of a 2% palladium catalyst on a carbon support. A quantity

of 4 mL per hour of CFC-113a (Cl_3CCF_3) was conducted to this reactor along with a mole ratio of hydrogen gas to CFC-113a equal to 10.0. The reactor effluent was characterized by GC/MS. The data shown in Table II were obtained by maintaining the inlet section of the reactor containing the ruthenium catalyst at 225°C. The temperature of the outlet section of the reactor was varied. The data provide proof-of-principle that HFC-356 can be synthesized in this manner. Moreover, the primary byproduct of this reactions, F_3CCH_3 (HFC-143a) is a desirable third-generation refrigeration fluid.

TABLE II - Area % from GC/MS

	139°C	149°C	175°C	193°C	231°C	247°C
356[1]	31.05	36.06	37.77	42.79	54.51	62.43
346[2]	23.3	29.86	28.35	21.67	5.74	0
143a	18.85	23.33	21.28	23.55	26.68	27.39
133a		5.87	7.35	8.02	13.06	10.18
123		4.09	5.25	3.97	0	0

[1]HFC-356mff
[2]HCFC-346 ($CF_3CClHCH_2CF_3$)

Example 3 - Synthesis of HFC-356mff from CFC-123

A precursor to HFC-356mff was synthesized from CFC-123 using the microreactor of Example 1. The GC/MS results show a high yield to the four-carbon intermediate. The data shown in Table III provide the conversion and selectivity as functions of temperature. The reactant was CFC-123 and the catalyst was 10% ruthenium on alumina. These data were obtained at 2 LHSV, 10:1 H_2:CFC-123 molar ratio, and 30 psig pressure as a function of temperature. It can be clearly seen that HCFC-336 ($CF_3CHClCHClCF_3$) can be produced in this manner. Furth r refinements in th pr cess conditi ns

will lead to an increasing concentration of this product. Because the internal carbon atoms are chiral, two peaks are obtained for the products; one peak is the meso compound while the other is a d/l pair. This intermediate can be subjected to catalytic hydrodechlorination to obtain the desired HFC-356mff.

TABLE III - Selectivities and Conversion

	209°C	245°C	265°C	404°C
HFC-1336[1]	2.9	2.7	4.4	12.8
HCFC-336	32.2	53.2	47.4	7.9
Coupling Selectivity	35.1	55.9	51.8	20.7
HCFC-123 Conversion	6.5	16.5	18.6	72.1

[1]HFC-1336 ($F_3CCH{=}CHCF_3$)

Example 4 - Synthesis of HFC-55-10 from CFC-215

HFC-55-10 was synthesized from CFC-215 using the microreactor of Example 1. CFC-215 was the reactant and the catalyst was 15% ruthenium on alumina. The data shown in Figure 1 represent the total ion current (TIC) from the GC/MS at a 197°C maximum reactor temperature. Figure 2 shows the MS fragmentation pattern for the $CF_3CF_2CCl{=}CClCF_2CF_3$ intermediate. Both of the peaks between 12.5 and 14 minutes have essentially the same fragmentation pattern, and have been assigned to the cis and trans isomers. Figure 3 provides an analysis of the MS fragmentation pattern to verify the intermediate product composition. The GC/MS results show a high yield to CFC-151-10, which is the desired four-carbon intermediate. These data were obtained at 0.1 LHSV, 10:1 H_2:CFC-215 m lar rati , and

300 psig pressure as a function of temperature. It can be clearly seen that a high yield of CFC-151-10 can be obtained. Further refinements in the process conditions will lead to an increasing concentration of this product.

The synthesis of HFC-55-10 was demonstrated by increasing the peak reactor temperature to 269°C. the catalyst provided significant hydrogenation and hydrodechlorination activity at this temperature to convert the intermediate CFC-151-10 to HFC-55-10. The data shown in Figure 4 prove that we have prepared the HFC-55-10 by this technique. The mass fragmentation pattern in Figure 5 can be assigned to this product. The peak at 8.6 minutes was identified as HFC-151-10 ($CF_3CF_2CH{=}CHCF_2CF_3$). This product can also be hydrogenated to HFC-55-10.

CLAIMS

We claim:

1. A process for preparing the fluorine-containing product $RCF_bH_{c+a-1}H_{f+d-1}F_eCR'$ by coupling two chlorine-containing reactants, $RCCl_aF_bH_c$ and $R'CCl_dF_eH_f$, in the presence of hydrogen and a first catalyst, and further treating the coupled product with hydrogen or a fluorinating agent, optionally in the presence of a second catalyst, to form the fluorine-containing product, wherein R and R' are chosen from the group consisting of halogens, halogenated hydrocarbons, and hydrocarbons, and at least one of R and R' contains fluorine, a and d are integers from 1 to 3, b, c, e, and f are integers from 0 to 2, the sum of a, b, and c is 3, and the sum of d, e, and f is 3.

2. The process of Claim 1 wherein the fluorine-containing product are chosen from the group consisting of $F_3C\text{-}CH_2\text{-}CH_2\text{-}CF_3$, $F_2CH\text{-}CHF\text{-}CHF\text{-}CHF_2$, $HF_2C\text{-}CHF\text{-}CHF\text{-}CF_2H$, $F_3C\text{-}CHCl\text{-}CH_2\text{-}CF_3$, $F_3C\text{-}CF_2\text{-}CF_2\text{-}CF_3$, $F_3C\text{-}CCl_2\text{-}CH_2\text{-}CF_3$, $F_3C\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CF_3$, $F_3C\text{-}CF_2\text{-}CHF\text{-}CHF\text{-}CF_3$, $F_3C\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}CF_3$, $F_3C\text{-}CH_2\text{-}CHF_2$, $F_3C\text{-}CF_2\text{-}CH_2\text{-}CH_2\text{-}CF_2\text{-}CF_3$, $ClF_2C\text{-}CF_2\text{-}CH_2\text{-}CH_2\text{-}CF_2\text{-}CF_2Cl$, and $HF_2C\text{-}CF_2\text{-}CH_2\text{-}CH_2\text{-}CF_2\text{-}CF_2H$.

3. The process of Claim 1 wherein the chlorine-containing reactants are chosen from the group consisting of $FCl_2C\text{-}CClF_2$, $F_3C\text{-}CCl_3$, $F_3C\text{-}CF_2\text{-}CCl_3$, $F_3C\text{-}CF_2\text{-}CHCl_2$, $ClCF_2CF_2Cl_3$, CF_2Cl_2, $F_3C\text{-}CHCl_2$, and $F_3C\text{-}CH_2Cl$.

4. The process of Claim 1 wherein the first catalyst is chosen from the group consisting of a group VIII metal chosen from the group consisting of nickel, ruthenium, rhodium, palladium, osmium, iridium, platinum, iron, or cobalt and optionally dispersed on a high surface area support chosen from the group consisting of alumina, carbon, chromium oxid , chromium oxyfluoride, chromium fluorid .

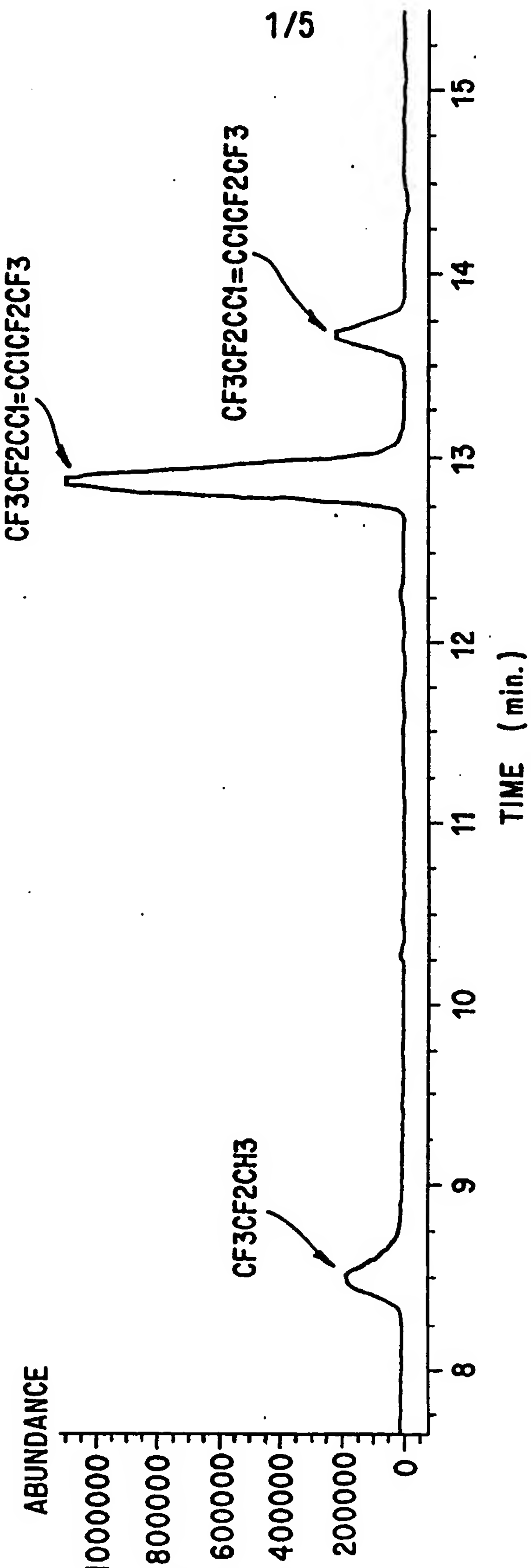
5. The process of Claim 4 wherein the first catalyst is reduced ruthenium catalyst dispersed on a high surface area support chosen from the group consisting of alumina and carbon.

6. The process of Claim 1 wherein the fluorinating agent is chosen from the group consisting of hydrogen fluoride, uranium fluoride, elemental fluorine, potassium fluoride, sodium fluoride, and cesium fluoride.

7. The process of Claim 1 wherein the second catalyst is chosen from the group consisting of group VIII metals chosen from the group consisting of platinum, cobalt, nickel, iridium, ruthenium and palladium, optionally modified by a promoter chosen from the group consisting of rhenium, iridium, cobalt, and nickel, and optionally modified by an attenuator chosen from the group consisting of sulfur, germanium, or tin.

8. The process of Claim 1 wherein R and R' are chosen from the group consisting of $-CF_3$, $-CCl_2F$, $-CF_2CF_3$, $-CF_2CF_2CF_3$, $-F$, $-Cl$, chlorine-containing alkyl groups, fluorine-containing alkyl groups, chlorine-containing aromatic compounds, and fluorine-containing aromatic compounds.

9. The process of Claim 1 wherein the two chlorine-containing reactants are combined in the presence of hydrogen and a catalyst to form at least one intermediate, $RCF_gH_hCl_iCl_jH_kF_lR'$, and wherein the intermediate is subsequently treated in the presence of an optional second catalyst with either a fluorinating agent, or with hydrogen and a catalyst to form the fluorine-containing product, wherein the sum of g, h, and i is an integer from 1 to 2, the sum of j, k, and l is an integer from 1 to 2, g, h, i, j, k, and l are int gers from 0 to 1.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CF3CF2CCl=CClCF2CF3
CF3CF2CH3
ABUNDANCE
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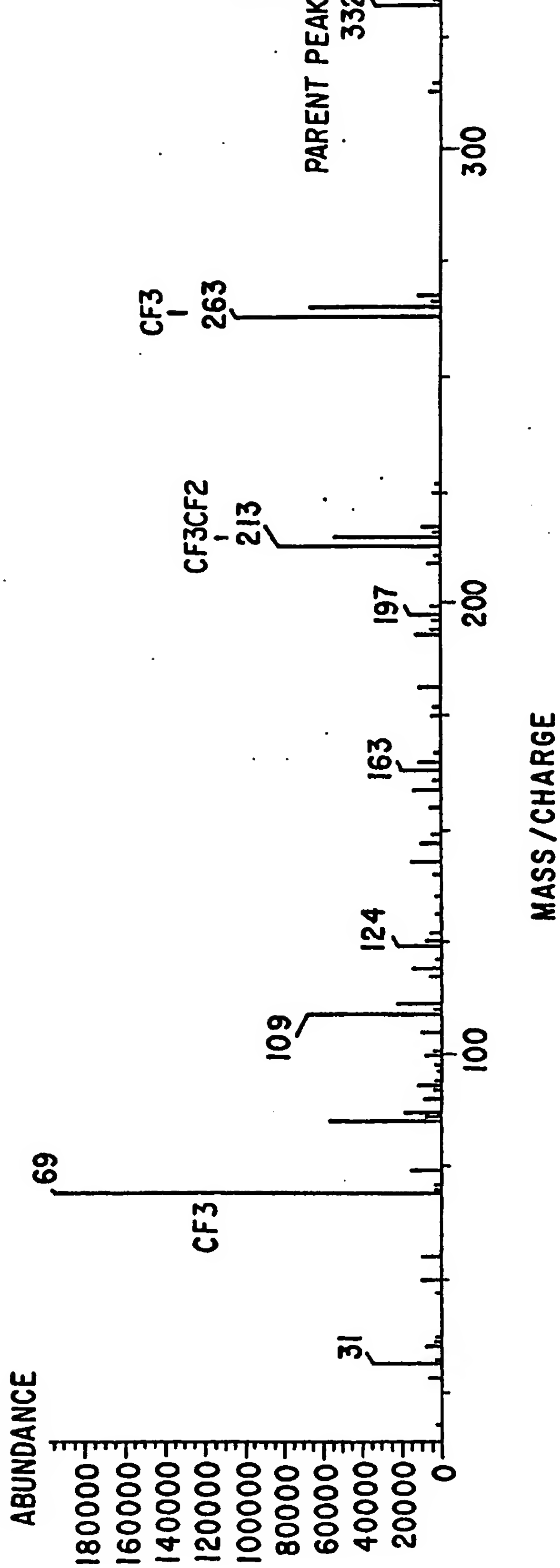
800000
600000
400000
200000
0
8
9
10
11
12
13
14
15
TIME (min.)

FIG.1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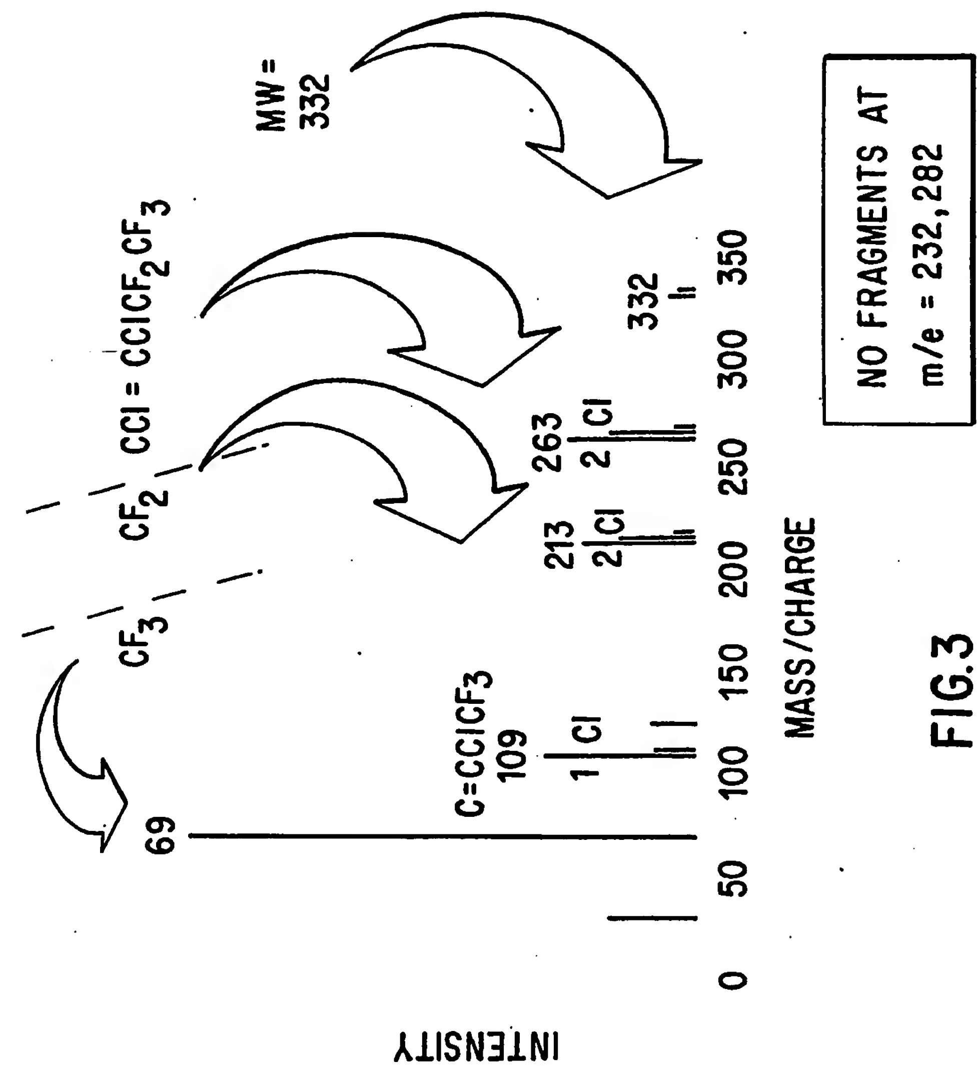
160000
140000
120000
100000
80000
60000
40000
20000
0
31
CF3
69
100
109
124
163
197
200
CF3CF2
213
CF3
263
300
PARENT PEAK
332
MASS/CHARGE

FIG.2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CF_3
CF_2
$CCl = CClCF_2CF_3$
69
$C{=}CClCF_3$
109
1 Cl
213
2 Cl
263
2 Cl
332
0
50
100
150
200
250
300
350
MASS/CHARGE
INTENSITY
NO FRAGMENTS AT
m/e = 232, 282

FIG.3

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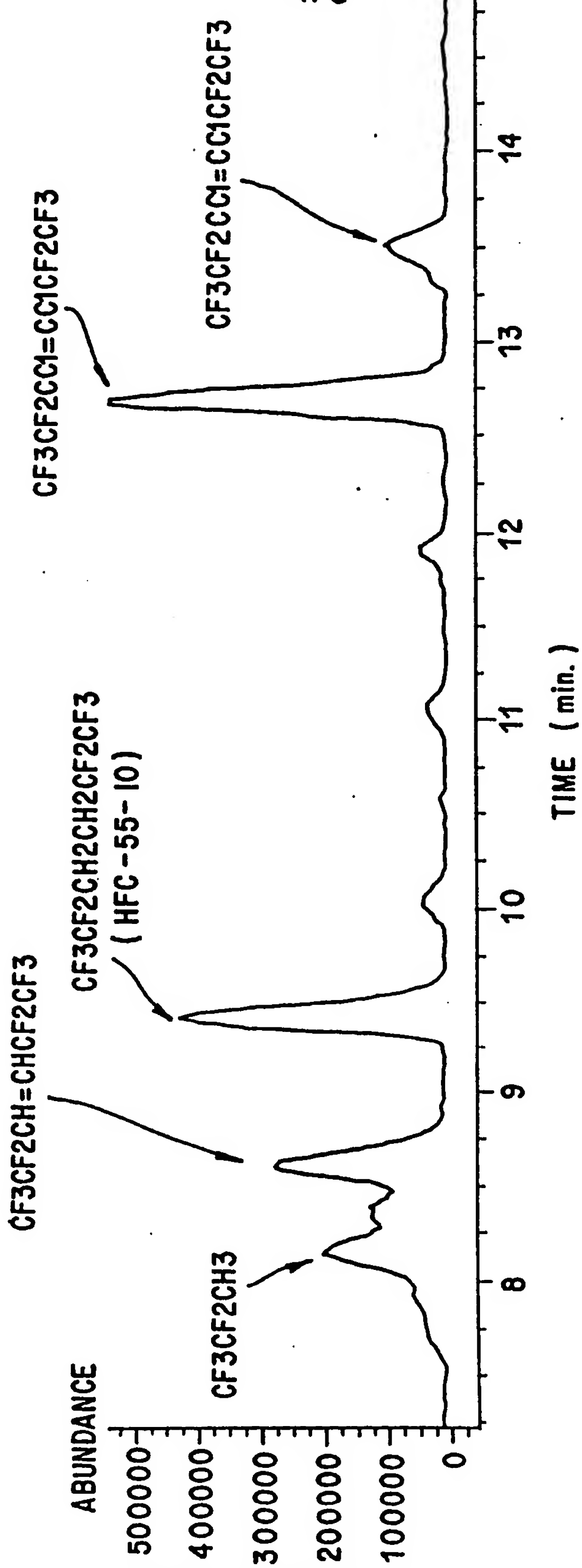
ABUNDANCE
500000
400000
300000
200000
100000
0
8
9
10
11
12
13
14
TIME (min.)
CF3CF2CH3
CF3CF2CH=CHCF2CF3
CF3CF2CH2CH2CF2CF3
(HFC-55-10)
CF3CF2CCl=CClCF2CF3
CF3CF2CCl=CClCF2CF3

FIG. 4

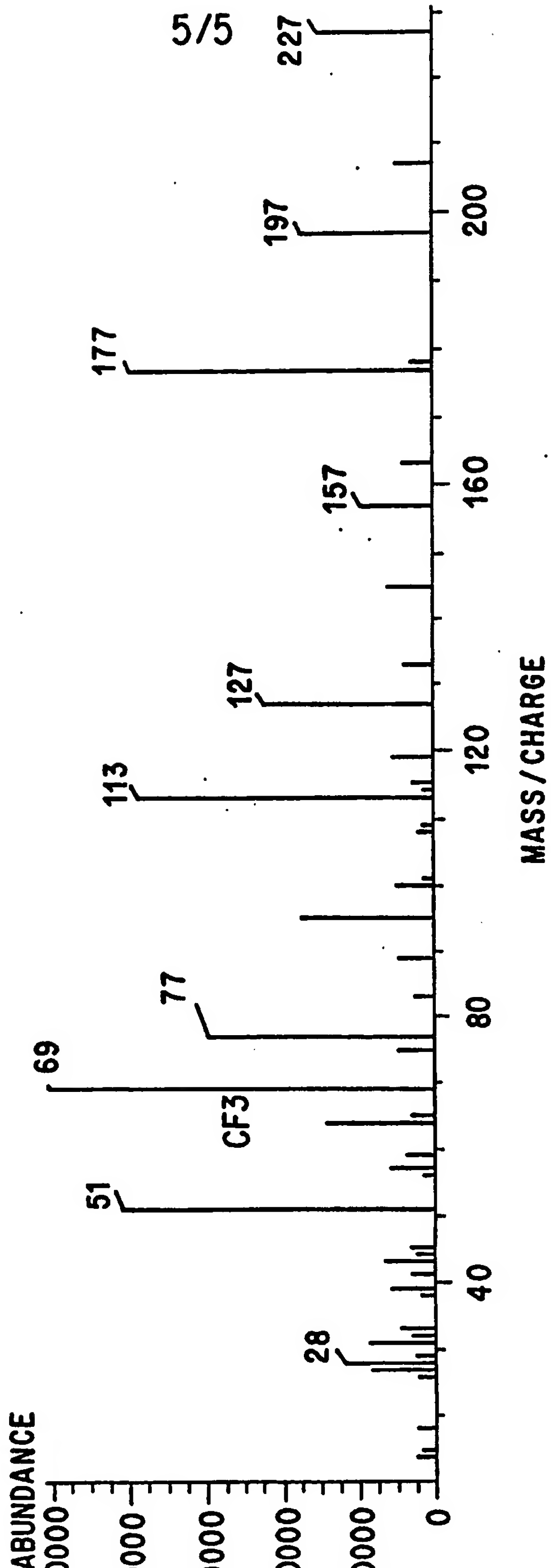
ABUNDANCE
50000
40000
30000
20000
10000
0
28
51
CF3
69
77
113
127
157
177
197
227
40
80
120
160
200
MASS/CHARGE

FIG.5

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 94/08986

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C07C19/08 C07C17/26 C07C17/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	EP,A,0 571 920 (HOECHST) 1 December 1993 see the whole document	1-5,7-9
P,X	WO,A,93 23354 (BAYER) 25 November 1993 see the whole document	1-4,7-9
Y	EP,A,0 499 984 (DAIKIN) 26 August 1992 see the whole document	1-9
Y	EP,A,0 442 087 (BAYER) 14 February 1990 see the whole document	1-9

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
28 November 1994	-8. 12. 94

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3016	Zervas, B

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inter. nal Application No
PCT/US 94/08986

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0571920	01-12-93	JP-A- 6056714	01-03-94
WO-A-9323354	25-11-93	DE-A- 4215876	18-11-93
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		CA-A- 2061234	17-08-92
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		DE-D- 59003798	20-01-94
		ES-T- 2059976	16-11-94
		JP-A- 4211026	03-08-92